

Organic cations controlling nuclearity of copper(II) 2,5-pyridinedicarboxylates

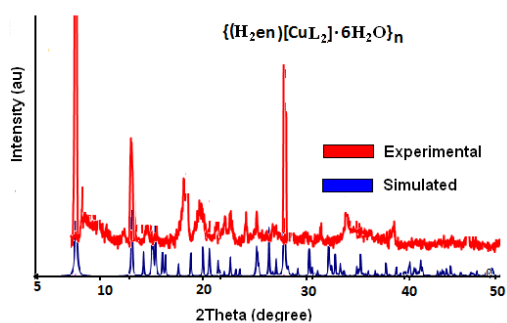
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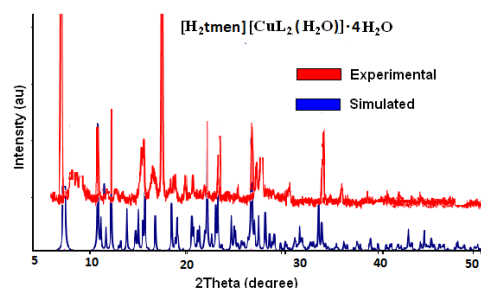
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Supplementary data:

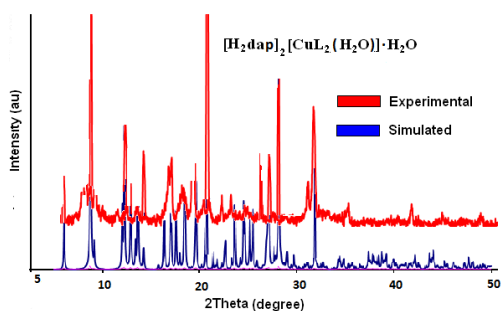
[A] Powder diffraction pattern of the complexes:



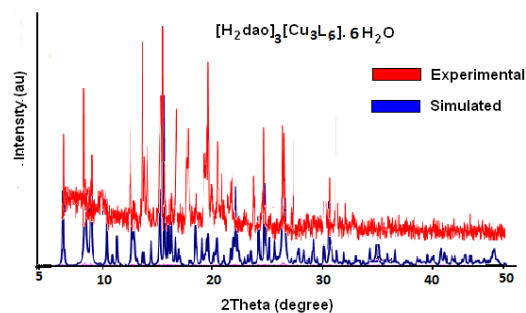
Complex 1



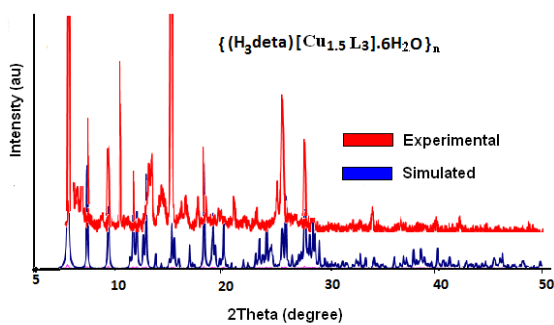
Complex 2



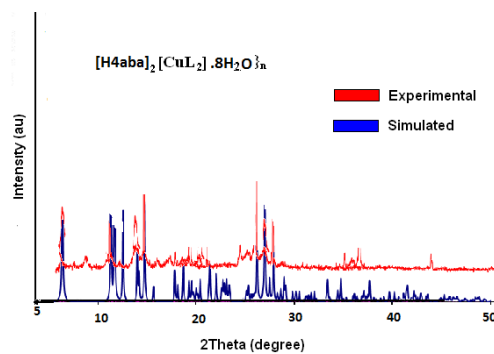
Complex 3



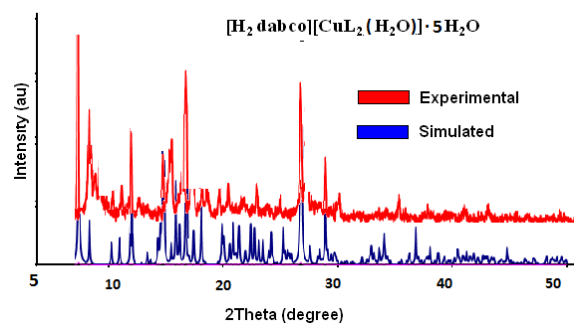
Complex 4



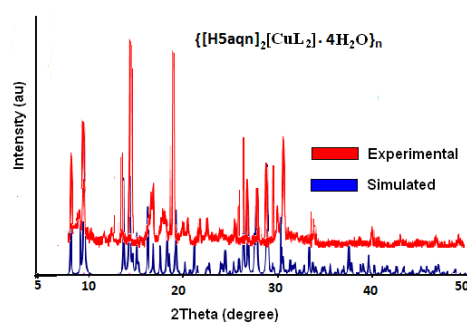
Complex 5



Complex 6

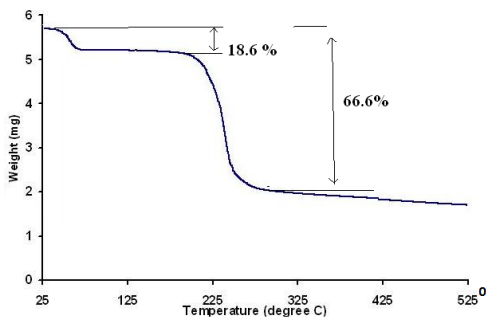


Complex 7

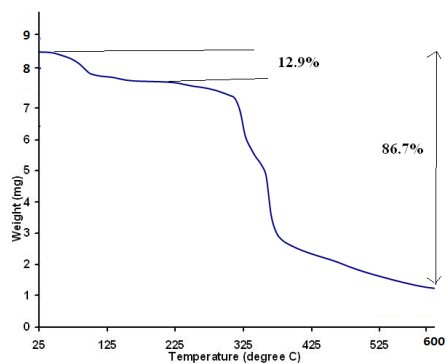


Complex 8

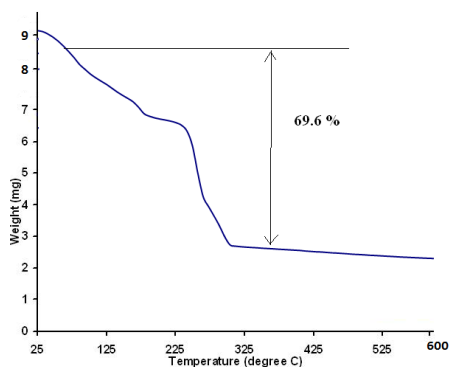
[B] Thermogram of the complexes:



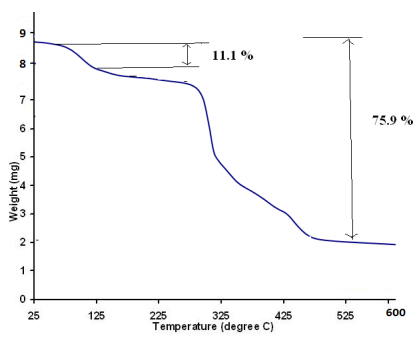
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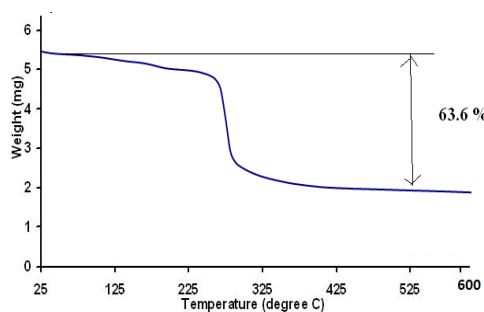
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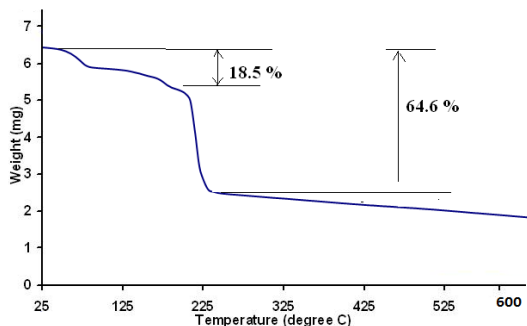
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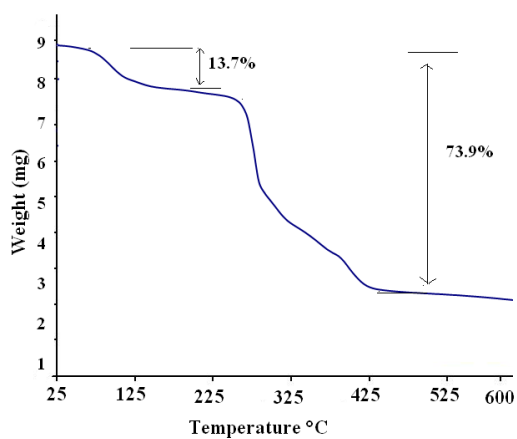
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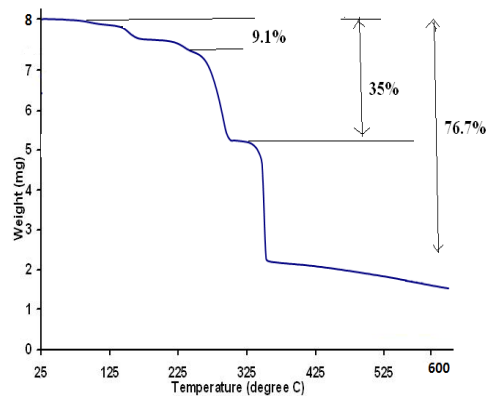
Complex 5



Complex 6

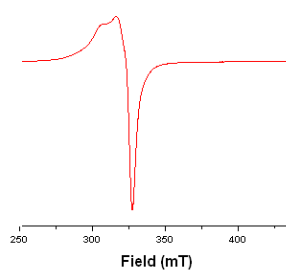


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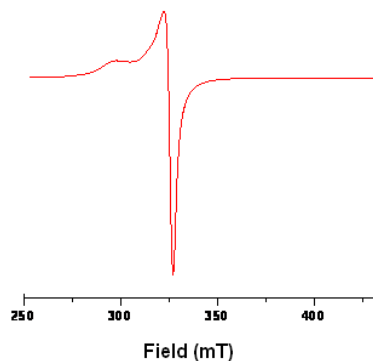


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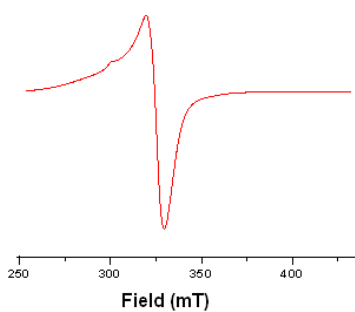
[C] EPR Spectra recorded in solid state central field at 3200 G:



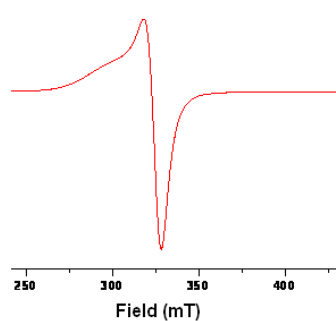
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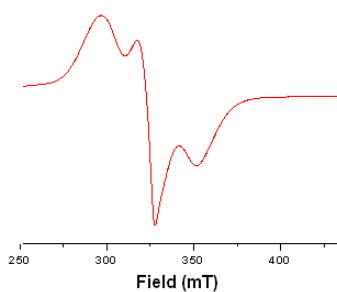
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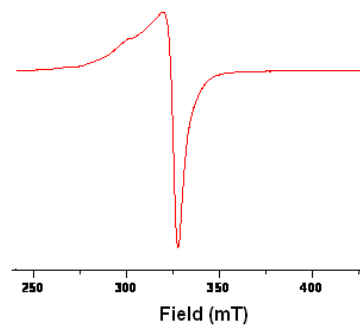
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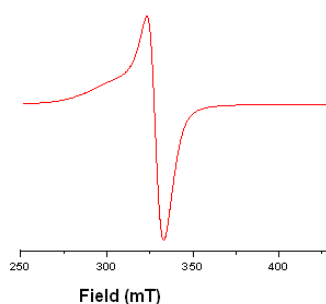
Complex 4



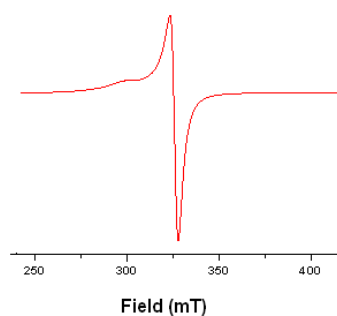
Complex 5



Complex 6



Complex 7



Complex 8

[E] Hydrogen bond parameters for the complexes **1-8**:

Compound	D-H...A (symmetry)	$d_{D-H}(\text{Å})$	$d_{H...A}(\text{Å})$	$d_{D...A}(\text{Å})$	$\angle D-H...A(^{\circ})$
{(H₂en)[CuL₂] ·6H₂O}_n (1)	N(2)-H(2B)...O(4) [2-x,1-y,-z]	0.89	2.10	2.921(4)	153
	N(2)-H(2C)...O(5) [x,1+y,z]	0.89	2.05	2.877(5)	155
	N(2)-H(2A)...O(6) [x, y, z]	0.89	2.21	3.037(5)	154
	O(6)-H(6B)...O(3) [1-x,1-y,-z]	0.94(4)	1.75(4)	2.688(5)	178(6)
	O(6)-H(6A)...O(5) [x, y, z]	0.95(5)	1.86(5)	2.807(5)	170(7)
	O(7)-H(7A)...O(2) [1-x,-y,1-z]	0.93(6)	1.95(6)	2.796(5)	150(6)
	O(7)-H(7B)...O(6) [x, y, z]	0.95(7)	1.98(6)	2.926(5)	173(7)
[H₂tmen][CuL₂ (H₂O)]·4H₂O (2)	N(3)-H(3N)...O(3) [2-x, 1-y, 1-z]	0.88(6)	1.85(6)	2.726(6)	174(6)
	N(4)-H(4N)...O(7) [1+x, -1+y, 1+z]	0.94(7)	1.71(7)	2.646(6)	179(10)
	O(9)-H(8AA)...O(11) [1-x, 1-y, 1-z]	0.96(5)	2.11(7)	2.955(6)	146(9)
	O(9)-H(8AB)...O(8) [-1+x, y, z]	0.95(6)	1.76(7)	2.716(5)	175(8)
	O(10)-H(10B)...O(12) [x, y, z]	0.87(9)	2.15(8)	2.878(11)	142(9)
	O(11)-H(9AA)...O(4) [-1+x, y, z]	0.95(6)	1.88(6)	2.812(8)	166(7)
	O(12)-H(12B)...O(13) [x, y, z]	0.96(15)	2.00(19)	2.914(10)	158(10)
	O(13)-H(13B)...O(4) [-1+x, y, z]	0.94(6)	1.86(6)	2.796(8)	172(9)
O(13)-H(13A)...O(9) [-x, 1-y, -z]	0.96(12)	1.90(13)	2.818(8)	159(17)	
[H₂dap]₂ [CuL₂(H₂O)]·H₂O (3)	N(3)-H(3A)...O(10) [-1+x,y,z]	0.89	1.92	2.811(3)	174
	N(3)-H(3B)...O(7) [-x,-y,-z]	0.89	1.88	2.761(3)	169
	N(3)-H(3C)...O(6) [x, y, z]	0.89	2.48	3.252(3)	146
	N(4)-H(4A)...O(4) [1-x,1-y,1-z]	0.89	1.91	2.797(3)	171
	N(4)-H(4C)...O(3) [x, 1+y, z]	0.89	1.94	2.762(3)	154
	O(9)-H(9C)...O(8) [-x, -y,-z]	0.91(3)	1.89(3)	2.744(3)	157(3)
	O(9)-H(9D)...O(4) [x,1-y,-z]	0.91(3)	1.87(3)	2.757(3)	165(3)
	O(10)-H(10C)...O(6) [x, y, z]	0.94(4)	1.96(4)	2.876(3)	166(4)
[H₂dao]₃ [Cu₃L₆]·6H₂O (4)	N(4)-H(4A)...O(13) [1-x,1-y,1-z]	0.89	1.97	2.798(4)	155
	N(4)-H(4B)...O(10) [2-x,1-y,1-z]	0.89	1.98	2.861(4)	169
	N(5)-H(5A)...O(19) [-x,1-y,-z]	0.89	2.00	2.872(4)	167
	N(5)-H(5B)...O(12) [-x,1-y,-z]	0.89	1.98	2.843(4)	164
	N(6)-H(6A)...O(7) [x, y, z]	0.89	1.88	2.766(4)	171
	N(6)-H(6B)...O(15) [x, y, z]	0.89	1.89	2.762(4)	165
{(H₃deta) [Cu_{1.5}L₃]·6H₂O}_n (5)	N(4)-H(4A)...O(7) [x, y, z]	0.89	2.23	2.967(6)	140
	N(4)-H(4B)...O(6) [-1+x,y,z]	0.89	2.16	2.929(5)	144
	N(4)-H(4C)...O(14) [-x,1-y,1-z]	0.89	1.88	2.761(6)	172
	N(5)-H(5A)...O(15) [x, y, z]	0.90	1.94	2.830(6)	170
	N(5)-H(5B)...O(12) [x,-1+y,1+z]	0.90	1.81	2.691(4)	165
	N(6)-H(6A)...O(4) [1-x,1-y,1-z]	0.89	1.99	2.799(5)	151
	N(6)-H(6B)...O(4) [1-x,1-y,1-z]	0.89	1.83	2.697(6)	165
	N(6)-H(6C)...O(18) [x, y, z]	0.89	2.00	2.846(8)	159
[H₄aba]₂[CuL₂] ·8H₂O}_n (6)	N(2)-H(2A)...O(8) [-1/2+x, 1/2-y, z]	0.89	1.99	2.868(4)	171
	N(2)-H(2B)...O(3) [-1/2+x,1/2-y, 1+z]	0.89	1.91	2.769(4)	162
	O(5)-H(5OB)...O(2) [x, y, z]	0.95(9)	2.24(9)	3.025(7)	139(8)
	O(6)-H(6OA)...O(3) [1/2-x, 1/2+y,1-z]	0.96(4)	1.80(4)	2.752(5)	174(4)
	O(7)-H(7OA)...O(4) [x, y, -1+z]	0.93(3)	1.88(3)	2.780(5)	163(5)
	O(7)-H(7OB)...O(8) [x, y, z]	0.95(6)	1.95(6)	2.861(5)	162(5)
	O(8)-H(8OB)...O(6) [x, y, z]	0.94(6)	1.89(5)	2.820(6)	167(5)
N(3)-H(3N)...O(7) [1-x, -y, -z]	0.96(5)	1.61(5)	2.564(6)	172(5)	

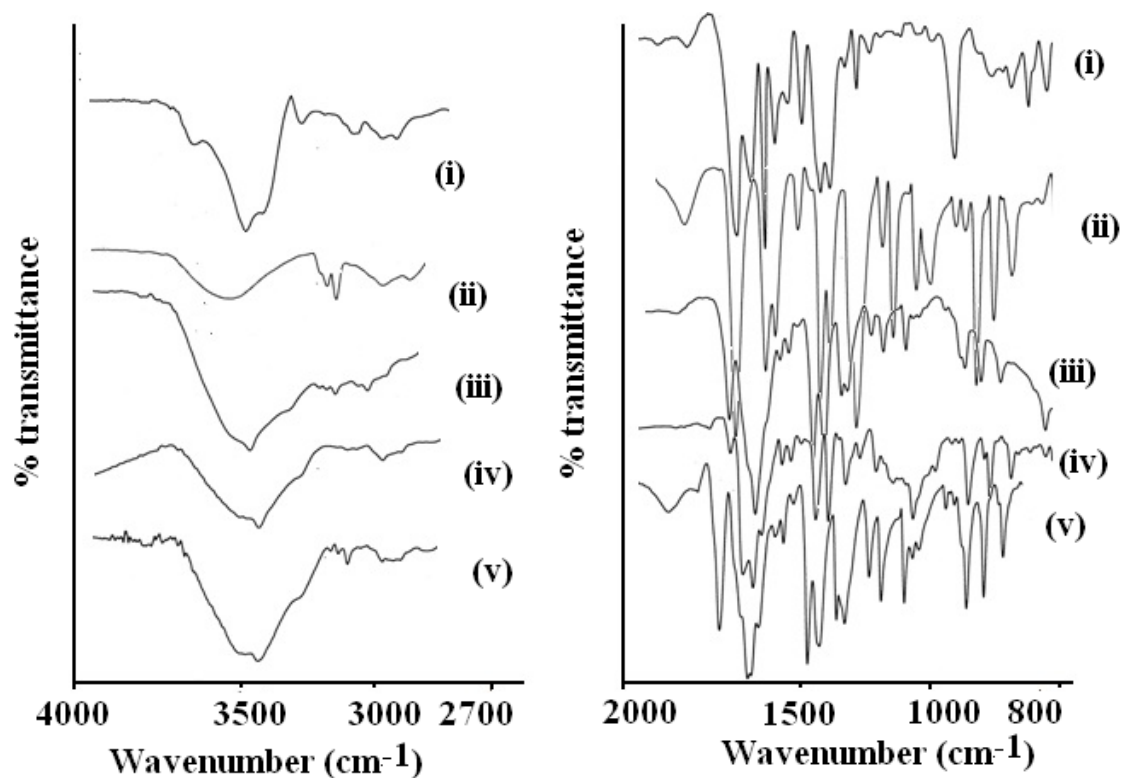
[H ₂ dabco] [CuL ₂ (H ₂ O)] ·5H ₂ O (7)	N(4)-H(4N)···O(3) [-x, 1-y, 1-z]	0.99(6)	1.77(6)	2.711(7)	157(6)
	O(9)-H(9OB)···O(4) [1+x, y, z]	0.94(5)	1.82(4)	2.752(6)	171(6)
	O(9)-H(9OA)···O(12) [1-x, 1-y, -z]	0.96(7)	1.87(5)	2.755(7)	153(9)
	O(10)-H(10C)···O(3) [x, y, z]	0.91(10)	1.81(10)	2.721(7)	176(9)
	O(10)-H(10D)···O(11) [1-x, 1-y, 1-z]	1.00(9)	1.79(8)	2.751(7)	159(8)
	O(12)-H(12C)···O(10) [x, y, z]	0.96(13)	1.75(13)	2.703(9)	172(13)
	O(12)-H(12D)···O(13) [1-x, 1-y, 1-z]	0.97(3)	1.83(4)	2.772(11)	166(3)
	O(13)-H(13C)···O(14) [1-x, -y, 1-z]	0.97(11)	1.99(9)	2.775(9)	137(9)
	O(14)-H(14C)···O(2) [x, y, 1+z]	0.95(14)	1.84(13)	2.771(9)	165(8)
	N(3)-H(3N)···O(7) [1-x, -y, -z]	0.96(5)	1.61(5)	2.564(6)	172(5)
{[H ₅ aqn] ₂ [CuL ₂] ·4H ₂ O} _n (8)	N(4)-H(4N)···O(3) [-x, 1-y, 1-z]	0.99(6)	1.77(6)	2.711(7)	157(6)
	N(2)-H(2N)···O(3) [2-x, -y, 1-z]	0.95(4)	1.78(4)	2.722(6)	171(4)
	N(3)-H(3A)···O(5) [x, y, -1+z]	0.96(7)	2.16(7)	3.073(7)	157(7)
	N(3)-H(3B)···O(1) [x, y, z]	0.95(9)	2.27(8)	3.119(6)	150(5)

[F] Temperature range for the loss of different components of the complexes 1-8

Complex	Evaporation tem. Of lattice H ₂ O	Loss of organic cation / ligand (L)
{(H ₂ en)[CuL ₂]·6H ₂ O} _n (1)	50-80 °C Loss of six water molecules Exptal = 18.6 % Calcd = 19.1 %	222-271 °C Loss of one L leading to [(en)CuL] _n Exptal = 66.6 % Calcd = 65.5 %
[H ₂ tmen][CuL ₂ (H ₂ O)]·4H ₂ O (2)	50-225 °C Loss of four water molecules Exptal = 12.9 % Calcd = 12.0 %	222-600 °C Leading to CuO Exptal = 86.7 % Calcd = 87.1 %
[H ₂ dap] ₂ [CuL ₂ (H ₂ O)]·H ₂ O (3)	No distinction of water of crystallization could be made. Weight loss 63-306 °C to form [CuL] _n Exptal 70.2% Calcd. 69.6 In this case sample is hygroscopic and the water loss from very temperature was observed hence we calculated loss from 63 °C.	
[H ₂ dao] ₃ [Cu ₃ L ₆]·6H ₂ O (4)	75-107°C Experimental 11.5% Calcd. 5.7% (ambiguity may be due to simultaneous loss of amine also)	227-450°C The weight loss corresponds to loss of amine and partial loss of L and satisfy a composition [Cu ₃ O(L) ₂] Exptal: 75.9 % Calcd : 72%
{(H ₃ deta)[Cu _{1.5} L ₃]·6H ₂ O} _n (5)	Loss of six water, loss of deta and loss of two pyridinedicarboxylate 64-350°C Exptal: 63.6%; calcd. 66.7%	
[H ₄ aba] ₂ [CuL ₂]·8H ₂ O (6)	64-200°C Loss of eight water molecules Exptal. 18.5% calcd. 18.4%	212-225°C Loss of one pyridine dicarboxylate ligand and two molecules of 4-aminobenzyl amine leading to [CuL] _n Exptal: 64.6 % Cald. 66. 2%
[H ₂ dabco][CuL ₂ (H ₂ O)]·5H ₂ O (7)	58-200°C Loss of five water molecules Exptal: 13.7 % Cald. 14.6%	225-425°C Formation of [CuO _{0.5} L _{0.5}] _n Exptal: 73.9 % Cald. 75 .0%
{[H ₅ aqn] ₂ [CuL ₂]·4H ₂ O} _n (8)	70-150°C Loss of four water Molecules Exptal: 9.1 %	225-600°C Loss of aminoquinoline, and one pyridinedicarboxylate Leading to [CuL] _n

	Cald. : 9.6 %	Exptal: 76.7 % Cald. 75.0%
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[G] Effect of temperature on the IR signals of complex 6.



IR spectra of (i) 4-aminobenzylamine (ii) $\{H_2[CuL_2]\}_n$ (iii) Complex $[H4aba]_2[CuL_2] \cdot 8H_2O$ (6) (iv) Complex 6 heated at 75 °C for half an hr. (v) Complex 6 heated at 275 °C for half hr.